On the whole, the IR and NMR data are in agreement with a Pt–H bond trans to a group of low trans influence, as expected for a *trans*-N–Pt–H arrangement.

The stability of complex III, in comparison with that of the [Pt(N–C–N)H] species cited by van Koten,[3] is likely to be related to such an arrangement. In platinum chemistry, strong trans directors such as H prefer weak trans-influence ligands (e.g. N donors) opposite to them.[9,2d]

In the attempt to verify the ability of the mononuclear hydrido complex to act as a donor,[10] complex III was reacted with a solvato species [Pt(N–N–C)(S)][BF_4] (V) (S = CH_3COCH_3, H_2O) (eqs 3 and 4). The reaction product analyzes correctly for the dinuclear derivative VI;[11] in agreement, the mass spectrum (positive ion, FAB conditions) shows the molecular ion [M^+] at *m/z* 909.

$$[\mathrm{Pt(N{-}N{-}C)Cl}] + \mathrm{AgBF_4} \xrightarrow{\mathrm{S}} \underset{\mathbf{V}}{[\mathrm{Pt(N{-}N{-}C)(S)}][\mathrm{BF_4}]} \qquad (3)$$

$$[\mathrm{Pt(N{-}N{-}C)H}] + [\mathrm{Pt(N{-}N{-}C)(S)}][\mathrm{BF_4}] \rightarrow \underset{\mathbf{VI}}{[\mathrm{(N{-}N{-}C)Pt(\mu\text{-}H)Pt(N{-}N{-}C)}][\mathrm{BF_4}]} \qquad (4)$$

Whereas no evidence of a bridging hydride is given by the IR spectrum, this is proved unequivocally by the ^1H NMR spectrum. At room temperature (CD_2Cl_2), two signals are observed at δ −14.9 and at −15.95. For both signals the expected pattern (quintet, 1:8:18:8:1) is not fully resolved; however, the intensity ratio of the three central peaks (ca. 1:2:1) fits a dinuclear system. Once again the J_{Pt-H} values are large if compared with those observed in dinuclear platinum complexes with phosphorous ligands,[10a,b,12] as well as with those reported by van Koten.[3]

The presence of two signals (ca. 1:1, room temperature) in the hydrido region, taken together with the presence of more sets of signals for the protons of the organic ligand, supports the existence in solution of diastereoisomers. This is not surprising taking account of the complexity of a molecule, where the two [Pt(N–N–C)] moieties, each containing a six-membered cycle, are connected through the bridging hydrido. Further work is currently in progress to attain the separation of the isomers and their full characterization.

Although the palladium analogue of complex III has not been obtained from II, the isolation of the platinum hydride III may be relevant to the hypothesis that hydrido species are intermediates in reactions involving cyclopalladated molecules having nitrogen donors.[13]

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(11) Analytical data for IV are as follows: Color: orange-yellow. Yield: 70%. Dec pt: 205 °C. Anal. Calcd for $C_{36}H_{31}BF_4N_4Pt_2$: C, 43.37; H, 3.11; N, 5.62. Found: C, 42.77; H, 3.36; N, 5.64. ^1H NMR (CD_2Cl_2, room temperature, 300 MHz): δ −15.95 ($^1J_{Pt-H}$ = 880 Hz, ca. 1:2:1, ca. 0.5 H), −14.9 ($^1J_{Pt-H}$ = 936 Hz, ca. 1:2:1, ca. 0.5 H), 1.77 (d, $^3J_{H-H}$ = 7.2 Hz, ca. 1 H), [1.96 (d, $^3J_{H-H}$ = 7.5 Hz) + 1.99 (d, $^3J_{H-H}$ = 7.2 Hz), ca. 5 H], 4.60 (q, $^3J_{H-H}$ = 7.2 Hz, ca. 1 H), 4.67 (q, $^3J_{H-H}$ = 7.5 Hz, ca. 0.5 H), 4.73 (q, $^3J_{H-H}$ = 7.5 Hz, ca. 0.5 H), 6.7–10.8 (m, 22 H).

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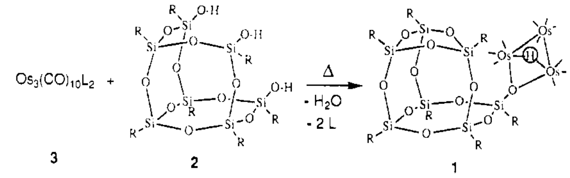
A Triosmium Cluster–Siloxane Cage Complex. Synthesis and Structure of $HOs_3(CO)_{10}[(\mu\text{-}O)Si_7O_{10}(C_6H_{11})_7]$

Silica-supported metal species are technologically important catalysts, but the metal–silica interaction is difficult to define at the atomic level. One active approach to the problem is the preparation and characterization of molecular complexes incorporating M_x–O_y–Si_z interactions as models for the catalytic materials.[1,2] Feher and co-workers[3] have shown that incompletely condensed silsesquioxane frameworks are effective models for silica surfaces. In view of the ongoing efforts to define the surface species formed from the interaction of $M_3(CO)_{12}$ (M = Os, Ru) with silica,[4-7] we have begun to examine the interaction of appropriate $M_3(CO)_{12}$ derivatives with silsesquioxanes. In this paper we report the isolation and structural characterization of the triosmium–silsesquioxane complex (μ-H)$Os_3(CO)_{12}$[(μ-O)-$Si_7O_{10}(C_6H_{11})_7$] (**1**), generated as shown in eq 1.



3 2 1 (1)

The reaction of the "lightly stabilized" cluster $Os_3(CO)_{10}$-$(C_8H_{14})_2$ (**3**)[8] with the trisilanol (c-$C_6H_7)_7Si_7O_9(OH)_3$ (**2**)[3a] was conducted in cyclooctene at 130 °C for 24 h, and complex **1** was isolated as a stable, yellow solid in 13% yield following chromatography.[9] The formulation of **1** was established by using

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(9) $(C_6H_{11})_7Si_7O_9(OH)_3$ (73 mg, 0.075 mmol) was placed in a Schlenk tube, which was then evacuated (oil pump) for 20 min. A cyclooctene solution of $Os_3(CO)_{10}(C_8H_{14})_2$ (80 mg, 0.075 mmol) was added under a nitrogen atmosphere, and the solution was heated in an oil bath at 130 °C for 24 h. The color turned from yellow to orange to brown. After removal of the solvent under reduced pressure, the residue was separated twice by preparative TLC (silica), eluting with a mixture of carbon tetrachloride/*n*-hexane (4:1). Several bands were separated, and the second fastest eluting yellow band corresponded to $HOs_3(CO)_{10}$[(μ-O)$Si_7O_{10}(C_6H_{11})_7$] (17 mg, 13%). Single crystals of **1** were obtained from dichloromethane/*n*-hexane at −10 °C for 7 days. The other products resulting from this reaction have not been definitively formulated, although it is clear (^1H NMR, MS) that reaction(s) of the cyclooctene ligand(s) are involved. *Note*: Since this paper was submitted, we have found that $Os_3(CO)_{12}$ and **2** react slowly (117 h) in refluxing octane to give **1** as the major TLC-mobile product in 28% isolated yield.

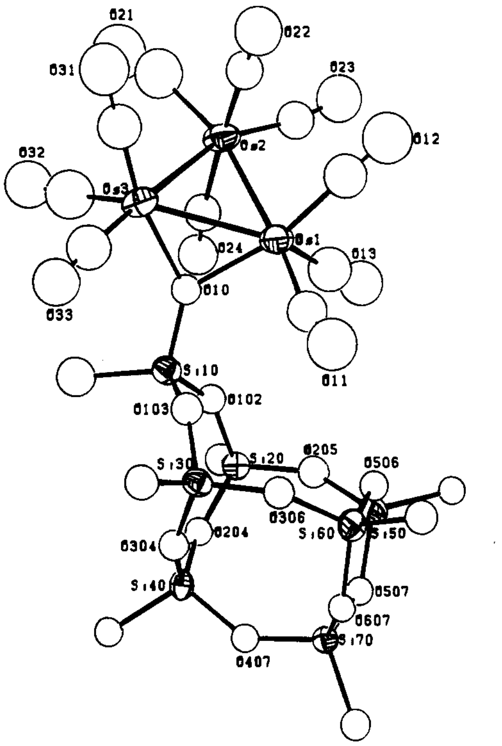

Figure 1. Molecular structure of $(\mu\text{-H})Os_3(CO)_{10}[(\mu\text{-O})Si_7O_{10}(C_6H_{11})_7]$ (**1**). For clarity the cyclohexyl rings have been deleted, except for the carbon atom directly linked to each silicon atom.

standard analytical techniques,[10] and the structure has been determined by a single-crystal X-ray diffraction study.[11]

The molecular structure of **1** is shown in Figure 1. The triosmium atom framework of **1** consists of a nearly isosceles triangle having two long edges (Os(2)–Os(3) = 2.828 (2) Å, Os(1)–Os(2) = 2.819 (2) Å) and one short edge (Os(1)–Os(3) = 2.789 (2) Å) and is similar to that found for the analogous cluster compound $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OSiEt}_3)$ (**4**).[7] The short bond in the Os_3 triangle is bridged by the $\mu\text{-OSi}_7O_{10}(C_6H_{11})_7$ ligand and presumably by the hydrogen atom (not located). The bridging oxygen atom O(10) serves as the linkage between the Os_3 cluster and the $\text{-Si}_7O_{10}(C_6H_{11})_7$ fragment, and the bond distances (O(10)–Si(10) = 1.63 (2) Å, O(10)–Os(1) = 2.13 (2) Å, and O(10)–Os(3) = 2.11 (2) Å) in the $Os_2(\mu\text{-O})Si$ ring are not significantly different from those in **4**. It is now apparent that the other substituents (alkyl vs siloxyl) attached to the supporting silicon center do not have a significant influence on the $Os_2(\mu\text{-O})Si$ dimensions.

The most striking change with respect to the silsesquioxane framework is the formation of the siloxane linkage Si(50)–O(506)–Si(60) by the cyclodehydration of two silanol groups from **2**. This produces an interesting pentacyclic Si_7O_{10} skeleton that has been previously observed[3a,c] but has not been crystallographically characterized until now.

Metrical data for the Si_7O_{10} cage do not deviate significantly from their normal ranges. As expected, all Si atoms have nearly tetrahedral coordination (106–110°) with internuclear Si–O distances of 1.61–1.65 (3) Å. The Si–O–Si bond angles span a range from 129 to 151°, but these also exhibit the expected trends. For example, the average Si–O–Si angle in the unique Si_5O_5 ring is slightly greater than that observed for the two fused Si_4O_4 rings that help to define the Si_3O_3 ring (145° vs 141°). The Si–O–Si bond angles in the Si_3O_3 ring are substantially more acute (129–134°), but are identical with the Si–O–Si angles observed for the two Si_3O_3 rings in $(c\text{-}C_6H_{11})_6Si_6O_9$.[12] They are also comparable to the ranges of values observed for the Si_3O_3 moieties in cyclosiloxanes[13] and cyclosilicate minerals.[14]

One interesting feature of the structure is that the Si_4O_4 ring defined by Si(10), Si(20), Si(30), and Si(40) adopts a folded conformation with the cyclohexyl groups on Si(10) and Si(40) located in a mutually "cis-diaxial" orientation. This requires a "flip" of the Si_4O_4 ring about O(102) and O(103) (relative to **2**), but places the Os_3 cluster away from the silsesquioxane framework in a nominally "equatorial" position. It is clear that silsequioxane frameworks are quite flexible.

Compound **1** does not react with water when heated at 55 °C for 1 h in a water/acetone/cyclohexane (1:4:3) solution. However, the fact that trisilanol **2** can be easily cyclodehydrated by reaction with **3** suggests that an important first step in reactions of metal carbonyls with noncalcined silica may be surface dehydration. This and other questions related to the formation and reactivity of complex **1** are under investigation.

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Supplementary Material Available: Tables of the details of the crystallographic data collection, atom coordinates, thermal parameters, bond distances, and bond angles (10 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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(10) Anal. $(C_{52}H_{78}H_{21}Si_7Os_3)$ C, H. Mass spectrum (^{192}Os, EI): m/z 1810 (M^+). ^1H NMR ($CDCl_3$, 20 °C): δ −12.56 (s, 1 H), 0.8 (vbr, m, 7 H), 1.25 (vbr, m, 35 H), 1.72 (vbr, m, 35 H). IR (C_6H_{12}), ν(CO): 2109 (w), 2070 (s), 2057 (m), 2022 (vs), 2001 (m), 1985 (m), 1953 (w) cm^{-1}.

(11) Compound **1** crystallizes in the monoclinic space group $P2_1/a$ with $a = 19.6594$ (11) Å, $b = 15.1406$ (8) Å, $c = 24.2560$ (13) Å, $\beta = 103.648$ (2)°, $V = 7016$ (2) $Å^3$, $Z = 4$, and $D_c = 1.710$ g cm^{-3}. Diffraction data (Mo Kα) were collected at 27 °C on an automated Syntex $P2_1$ diffractometer. A total of 3562 reflections with $I > 2.58\sigma(I)$ were corrected numerically for absorption ($\mu = 56.05$ cm^{-1}; maximum/minimum transmission factors = 0.489/0.251) and used to solve the structure by direct methods (SHELXS-86). Correct positions for osmium and silicon atoms were deduced from an E map. Subsequent least-squares refinements and difference Fourier synthesis (SHELX-76) revealed positions for the remaining non-hydrogen atoms. The osmium and silicon atoms were refined with anisotropic thermal coefficients, the remaining nonhydrogen atoms with independent isotropic coefficients, and the idealized hydrogen atoms with a common isotropic parameter. Final agreement factors were $R = 0.066$ and $R_w = 0.073$ for 384 variables.

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